Activity of phthalocyanine-sensitized TiO$_2$-anatase in photooxidation of sulfite ions

Maria Galbas, Agnieszka Banaszczyk, Gabriela Dyrda, Kszyżtof Szczegot, Rudolf Słota*

Opole University, Faculty of Chemistry, ul. Oleska 48, 45-095 Opole
e-mail: rslota@uni.opole.pl

Hybrid catalysts based on the TiO$_2$ matrix impregnated with Nd, Eu and Yb diphthalocyanines proved effective in oxidation of sulfite ions under irradiation with light from the UV-visible range. Micro- and nano-crystalline anatase powders were used in preparation of the photocatalysts, which were applied in the form of a suspension in the water phase. The reaction yield was found to depend on the phthalocyanine sensitizer used and the conditions of TiO$_2$ impregnation. The best results were obtained when micro-anatase impregnated with Yb-diphthalocyanine was used.

**Keywords:** TiO$_2$, anatase, phthalocyanine sensitizer, photooxidation, hybrid photocatalysts.

**INTRODUCTION**

Titanium dioxide has become one of the most popular and promising inorganic materials during the last decades of the XX century. Commonly used in production of pigments, cosmetics and pharmaceutics, TiO$_2$ was re-discovered for much more sophisticated applications, such as semiconductors or capacitors for electronics, photoactive elements for solar cells, catalysts and photocatalysts$^{1-3}$. As a chemically very stable and non-toxic solid material, titanium dioxide offers a range of important optoelectronic properties, i.a. semi-conductivity$^{4-6}$, photocatalytic activity$^4$, 7 and considerable photostability$^8$, 9. From among its three natural polymorphs only rutile and anatase have been considered for wide industrial application. Although rutile has proved thermodynamically more stable, however it is anatase which has displayed better photocatalytic activity and hence has received much more attention as a matrix for diverse catalytic systems than rutile does$^1$, 4, 6.

The band gap energy of anatase (3.2 eV) falls into the UV range of photonic energy and for this reason ultraviolet irradiation is necessary to (photo)activate its electronic system to create the reactive electron-hole pairs ($e^-$, $h^+$). Practically, photons of $\lambda > 400$ nm are not absorbed by TiO$_2$ and to enhance its light harvesting ability over the visual range some modifications must be introduced into the anatase matrix$^{10}$. The most simple way to extend the absorption range is to prepare TiO$_2$-dye composites, and there is a rich literature reporting on such systems. In the recent years novel anatase-based photocatalysts were developed involving phthalocyanine and porphyrin sensitizers$^7$, 11-16. These interesting hybrid systems proved effective in photodegradation of 4-nitrophenol, 2-propanol, polyethylene and polystyrene$^{5-8}$, 17-20. It is believed they may be very useful both in industrial catalysis as well as important components of environment control systems.

Titanium dioxide (anatase) has become a commercial product and an abundance of its varieties has been made available, as far as grain size and activity are concerned. However, for the reasons of dedicated research projects (e.g. photocatalysis) it is usually synthesized in laboratory scale according to the methods reported elsewhere$^{1-3}$, 5-7, 21-24. Practically, most of the TiO$_2$ syntheses are carried out using the methods based on the sol-gel technique$^{1-3}$, 24.

Phthalocyanines, MPC (M is a metal ion, Pc = C$_{32}$H$_{16}$N$_8$ is the phthalocyanine ligand) represent a group of interesting heteromacrocyclic dye-sensitizers particularly valued for their significant photochemical activity both in the UV and visible range$^6$. These compounds can be appropriately chemically modified so that one can tune their light absorption spectrum in a wide range (Fig. 1).

![Figure 1. Molecular and spectral properties of phthalocyanines. (a) Phthalocyanine macrocycle (Pc = C$_{32}$H$_{16}$N$_8$); (b) Metal complexes of phthalocyanine (MPC); (c) Electronic absorption spectra (UV-Vis)
In dye-sensitized photocatalysis the matrix of a solid semiconductor catalyst has been impregnated with a properly chosen colorant to enhance the light absorption performance and hence improve the photocactivity of such a system. In fact, there are two photosystems operating simultaneously, that of the matrix and the other one of the sensitizer. The efficiency of such hybrid photocatalyst depends on how far these two photosystems may “cooperate” in electron transfer throughout the matrix, thus effectively extending the lifetime of the electron-hole pairs ($e^-, h^+$). The principle of the cooperative mechanism in a TiO$_2$–phthalocyanine hybrid catalyst system has been presented in Figure 2.

![Figure 2](image)

The cooperative mechanism principle in a phthalocyanine-sensitized TiO$_2$ (anatase) based hybrid photocatalytic system

In previous reports dedicated to porphyrin and/or phthalocyanine impregnated anatase composites, the lanthanide diphthalocyanines (Fig. 1b), LnPc$_2$ (where Ln is a lanthanide metal 3+ ion), were found particularly effective as sensitizers of the TiO$_2$ matrix. On the other hand, in these hybrid systems, the microstructure of the anatase substrate was found to favor the microcrystalline TiO$_2$ over the nano-structured one, which would have emphasized the relevance of proper component selection in preparation of dye-sensitized semiconductor-based photocatalysts.

Effectiveness of diverse anatase-LnPc$_2$ composites applied in the form of suspension in water was confirmed in photooxidation of 4-nitrophenol and 2-propanol, and preliminary tests had pointed at the potential of these photocatalysts also in photoactivated degradation of other chemicals, including sulfur compounds. Therefore, in this work we report on our recent results regarding the activity of some chosen anatase-LnPc$_2$ hybrid catalysts in photooxidation of sodium sulfite (Na$_2$SO$_3$). A homogeneous (not photo-activated) process involving a water-soluble Co-tetrasulfophthalocyanine catalyst in which the sulfate ions ($SO_3^{2-}$) were effectively converted into sulfate ($SO_4^{2-}$) ions was demonstrated elsewhere.

Since under normal aerobic and dark conditions sulfate ions are relatively easy oxidized by water-dissolved oxygen, the principal objective of this study was to find out how much this reaction could be accelerated in a photocatalyzed process. On the other hand, this work was designed to demonstrate the general effectiveness of the anatase-LnPc$_2$ composites and the relevance of the search for similar hybrid systems.

**EXPERIMENTAL**

Commercial anatase (Tioxide Huntsman, 8 m$^2$/g BET, grain size range 0.15–0.5 μm) and home-prepared nanocrystalline anatase (grain size 15–40 nm) were used in preparations of the hybrid catalysts. The “nano” modification was synthesized from titanium tetra-isopropoxide by the sol-gel technique, following the literature reported procedure. The product was characterized by X-ray powder diffraclrtometry (XRD) and scanning electron microscopy (SEM). X’Pert Pro Analytical diffractrometer and JEOL JSM-5400 microscope were used to accomplish these analyses. Results have been presented in Figure 3.

The diphthalocyanines of Nd, Eu and Yb were synthesized in our laboratory (Faculty of Chemistry, Opole University) according to own method. Dichloromethane (DCM) and dimethylformamide (DMF), both of analytical grade, were purchased at Sigma-Aldrich, and used as supplied.

Optimum composition of the hybrid photocatalyst was determined based on a series of preliminary tests, and it was found similar to the value reported in a previous work. The anatase substrate was impregnated according to the procedure used there. For this reason a portion of 1.8 μmol (ca. 2 mg) of LnPc$_2$ was dissolved in 15 ml of DMF and/or dichloromethane in a round bottom flask and 1 g of TiO$_2$ was added. The mix was stirred for 5 h and afterwards the solvent was vacuum-evaporated and the solid residue, i.e. the TiO$_2$–LnPc$_2$ composite, was left to dry in air at room temperature. The green form of YbPc$_2$ in DMF (see Fig. 1c) was obtained by addition of 2 drops of concentrated H$_2$SO$_4$ directly into the solution yet before mixing with TiO$_2$. The studied samples were labeled as shown in Table 1.

Photoactivity of the catalysts was tested using a thermostated glass photoreactor ($V = 15 \text{ cm}^3$) presented in Figure 4. The hybrid catalyst (2.5–5.0 mg) was suspended in 10 cm$^3$ of 1×10$^{-3}$ M Na$_2$SO$_3$ water solution, and the mixture was irradiated under continuous stirring. Sanolux HRC 300–280 xenon arc lamp was used to illuminate the content of the photoreactor from a distance of 50 cm. The emission spectrum of the radiation source has been shown in Figure 5 and the estimated irradiance (mW/cm$^2$) of the sample determined at the quartz window of the photoreactor (2 cm above the suspension) was 0.18 for UV-B (280–315 nm), 1.1 for UV-A (315–400 nm) and 3.9 for the visible radiation (380–780 nm). Periodically, 2 ml of the suspension was taken, filtered and analyzed for the content of SO$_3^{2-}$. Classical iodometric analysis was applied for SO$_3^{2-}$ concentration greater than 1×10$^{-4}$ mol/dm$^3$ and smaller quantities were determined spectrophotometrically. The effectiveness of the tested

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Sample description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Na$_2$SO$_3$ (no catalyst added)</td>
</tr>
<tr>
<td>T-1</td>
<td>micro-TiO$_2$</td>
</tr>
<tr>
<td>T-2</td>
<td>nano-TiO$_2$</td>
</tr>
<tr>
<td>Nd-1</td>
<td>NdPc$_2$ (blue form in DCM)</td>
</tr>
<tr>
<td>Nd-2</td>
<td>NdPc$_2$ (green form in DCM)</td>
</tr>
<tr>
<td>Eu-1</td>
<td>EuPc$_2$ (blue form in DCM)</td>
</tr>
<tr>
<td>Eu-2</td>
<td>EuPc$_2$ (green form in DCM)</td>
</tr>
<tr>
<td>Yb-1</td>
<td>YbPc$_2$ (blue form in DCM)</td>
</tr>
<tr>
<td>Yb-2</td>
<td>YbPc$_2$ (green form in DCM)</td>
</tr>
<tr>
<td>Yb-3</td>
<td>YbPc$_2$ (green form in DCM)</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Under dark conditions, the sulfite ions have been oxidized only by molecular oxygen originally present in the water phase and addition of the bare TiO$_2$ substrates did not result in a faster reaction progress, Figure 6. The same was observed for the TiO$_2$–LnPc$_2$ composites (not shown). Moreover, the catalyst-free system appeared only slightly sensitive to the applied radiation. Both the micro- and nano-anatase bare substrates similarly showed some increased yield in sulfite oxidation upon irradiation, however this had become apparent only after longer illumination periods. After impregnation with the LnPc$_2$ sensitizer, photoactivity of the micro-TiO$_2$ matrix increased considerably, as reported in Figure 7, whereas the nano-anatase composites revealed no catalytic activity (compared to the catalyst-free system). Similar observation was made while studying the photooxidation of 4-nitrophenol in water, although in this case the nano-TiO$_2$ hybrid catalysts clearly showed some enhanced activity$^{26}$. Evidently, the nano-TiO$_2$ matrix may not be sufficiently activated by the sensitizer to catalyze the photooxidation of Na$_2$SO$_3$. Instead, the micro-anatase based hybrids appeared very effective here, and this fact would have indicated for the relevance of the sensitizer choice. As follows from
Figures 8 and 9, the most pronounced photocatalytic effect was achieved when the micro-anatase matrix was impregnated with YbPc₂.

The proper amount of the catalyst used to compose the suspension (10 ml) in the photoreactor was determined as 5.0 mg per feed, under the applied reaction conditions. When less catalyst was added (2.5 mg) the reaction run definitely slower, depending on the system, however no simple relation was found. As follows from the graph presented in Figures 8 and 9, the way of preparation of the hybrid catalyst may also be important. Namely, the best results were obtained always when the catalyst was obtained in DCM and for YbPc₂ also in acidified DMF (see Table 1). This may be related to the formation of the so-called green form of the LnPc₂ complex, which has been considered more photoactive as the blue-LnPc₂ compound\textsuperscript{12,28}. The green modification is typically formed by LnPc₂ complexes when dissolved in DCM and also in DMF containing some amount of acid, which is featured in their UV-Vis spectra (Fig. 1c). However, in the latter case only compounds of the heavier lanthanide metals (Sm-Lu) are sufficiently stable. Hence in our study, the green form in DMF was represented only by YbPc₂.

According to the published research, the mechanism of photooxidation by using TiO₂-phthalocyanine composites is based on the concept of conversion of molecular oxygen and water molecules present in the reaction system into reactive oxygen species (ROS) by the photoexcited TiO₂ matrix and the MPc sensitizer. These are primarily free radicals and ions, e.g. O₂⁻, O₂²⁻, HO⁻, HO₂⁻, however due to the peculiar photochemical activity of the phthalocyanine component generation of singlet oxygen, \( ^1 \text{O}_2(\Delta_g) \), may also be possible\textsuperscript{15}. In the explored systems, formation of ROS may be concluded from the comparison of the dark experimental results with those collected after irradiation. It can be seen, that there was only a little difference in the reaction rate between samples S (D) and S (R), whereas addition only of the bare TiO₂ catalysts distinctly accelerated the photooxidation of sulfi te ions, Figures 6 and 9. On the other hand, the considerable rise in photocatalytic oxidation yield demonstrated by the TiO₂–LnPc₂ loaded suspensions (Figs. 7–9) evidently complies with the co-operative mechanism proposed for such hybrid systems, not excluding the part of singlet oxygen species. Obviously, the only possible reaction product of sulfi te photooxidation have been sulfate ions (SO₄²⁻) as followed from the analyses carried out during the photochemical experiments, and the studied process involving hybrid TiO₂-LnPc₂ may hence be summarized as in the scheme presented below.

\[
\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{ROS} + \text{SO}_3^{2-} \xrightarrow{} \text{SO}_4^{2-}
\]
CONCLUSIONS

Lanthanide diphthalocyanines (LnPc2) effectively enhance the photochemical activity of the TiO2(anatase) matrix. Based on the results collected so far one may assume, that such systems bear a great potential to be practically applied as photocatalysts in diverse oxidation reactions. Their catalytic efficiency was proved in some important photo-activated processes. However, the data reported here for sulfit photooxidation emphasize the peculiar feature of the TiO2–LnPc hybrids to considerably accelerate even a reaction, which under aerobic conditions proceeds rather fast by itself, without a catalyst. In summary, our results would point at the effectiveness of the explored photocatalysts particularly in photo-mediated oxidation processes, involving electron acceptor sulfur species, as well as other compounds of this kind.

ACKNOWLEDGMENT

Maria Galbas is a recipient of a Ph. D. scholarship under a project funded by European Social Fund.

LITERATURE CITED

